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Facile resolution of constrained geometry indenyl-phenoxide ligation†

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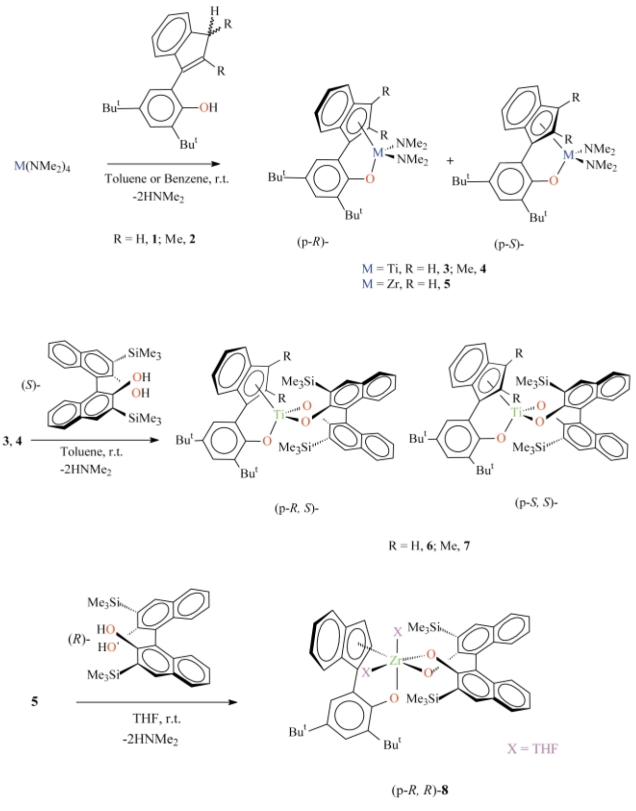
The 2-(inden-3-yl)phenoxide ligand can be resolved at both tetrahedral and octahedral Group 4 metal centers using chiral binaphthoxide ligands.

The chemistry of ansa metallocenes and constrained geometry ligands at Group 4 metal centers continues to be an important area of transition metal chemistry.[1] Of particular interest has been the design and application of chiral ligands of this type.[2] We have begun to study the coordination chemistry of 2-(indenyl)phenoxide ligands, which demonstrate a variety of coordination modes.[3] We wish to report here the resolution of this ligand system at both tetrahedral and an unusual octahedral Group 4 metal center.

Hydrocarbon solution of the ligands **1** and **2** (1 equiv.) react with the substrates [M(NMe_2)$_4$] (M = Ti, Zr)[4] to produce the corresponding bis(amides) **3–5** via activation of both the phenolic OH and indenyl CH bonds (Scheme).†‡ Structural studies of **3–5**,§ show the presence of both the (p-*R*) and (p-*S*) enantiomers within the unit cell due to the planar chirality generated via the indenyl coordination; Figure 1 shows (p-*R*)-**3**.



Scheme 1 Synthesis of compounds.

The remaining dimethylamido ligands in **3–5** can undergo protonolysis reactions with a variety of reagents. Reaction of the Ti compounds **3** or **4** with (*S*)-3,3′-bis(trimethylsilyl)-1,1′-binapthyl-2,2′-diol in aromatic solvents was found to initially produce a mixture of two diasteroisomers (**6** and **7**, Scheme 1) with well-resolved ligand signals within the NMR spectra. However, although at low temperatures a 50/50 mixture of isomers was observed for **6**, at ambient temperature the formation of a major isomer was found to take place. Isolated crystals from this reaction mixture were found to contain only one diastereoisomer, the thermodynamically more stable (p-*S*,*S*) form of **6**. The presence of the methyl substituents on the indenyl ring of **7** does not appear to allow isomerization and a 50/50 mixture is maintained even at 100 °C for days. Crystallization, however, did lead to the pure (p-*S*,*S*) form of **7** (Figure 2). In previous studies of pseudo-tetrahedral *rac*-bis(indenyl) ligand systems it has been shown that (*S*)-binapthoxide ligands lead to a preferential (p-*S*) coordination of the indenyl rings.[5] The change in chirality of the chelated indenyl-phenoxide ligand cannot occur via simple phenoxide dissociation. Instead "flipping" of the indenyl ring must occur. We believe this occurs via a reversal of the process that leads to **3** and **4**. Specifically it seems reasonable to propose reversible protonation of the indenyl ring can occur by the dimethylamine generated within the reaction. There is precedence for such a process in the interconversion of *mer*- and *rac*-bis(indenyl) systems.[6] In the case of the 2,3-dimethyl-indenyl ligand, however, this process cannot lead directly to ring-flipping as the proton has to be abstracted from the same face to which it was originally delivered.

The reaction of **5** with (*R*)-3,3′-bis(trimethylsilyl)-1,1′-binaphthyl-2,2′-diol also gave an initial 50/50 mixture of

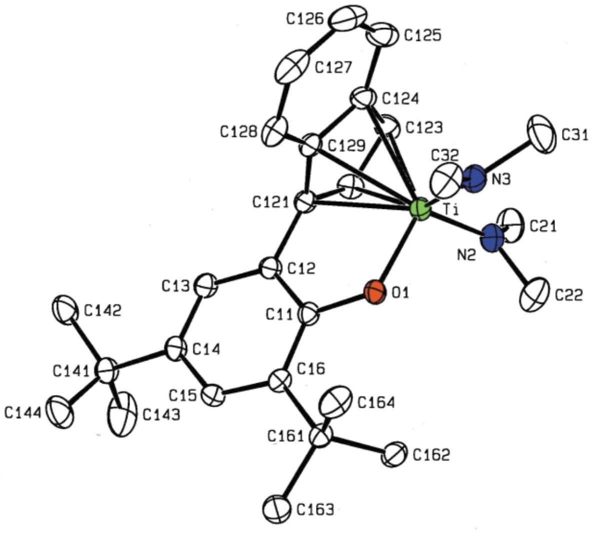


Fig. 1 Selected bond distances (Å) and angles (°) for **3**; (p-*R* form shown) Ti–O(1) 1.895(1), Ti–N(2) 1.905(2) ,Ti–N(3) 1.913(2), Ti–C(121) 2.366(2), Ti–C(122) 2.381(2), Ti–C(123) 2.380(2), Ti–C(124) 2.417(2), Ti–C(129) 2.405(2), O(1)–Ti–N(2) 107.07(6), O(1)–Ti–N(3) 100.22(6), N(2)–Ti–N(3) 102.02(6).

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† Electronic supplementary information (ESI) available: synthesis of compounds **1–8** and ORTEP views of**4**,**5** and **6**. See http://www.rsc.org/suppdata/cc/b2/b212724e/

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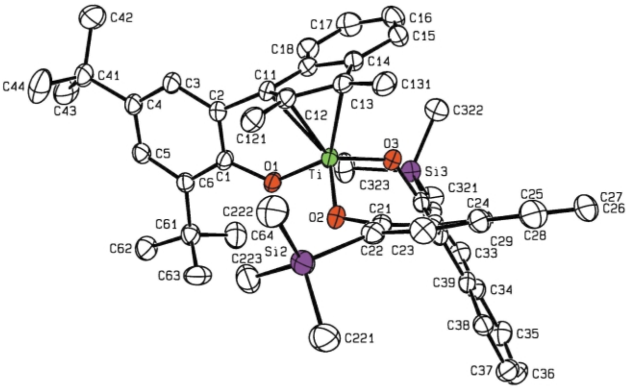

Fig. 2 Selected bond distances (Å) and angles (°) for (p-*S*,*S*)-**7**: Ti–O(1) 1.864(2), Ti–O(2) 1.862(2), Ti–O(3) 1.866(2), Ti–C(11) 2.310(3), Ti–C(12) 2.318(3), Ti–C(13) 2.361(3), Ti–C(14) 2.522(3), Ti–C(19) 2.472(3), O(1)–Ti–O(2) 96.91(9), O(2)–Ti–O(3) 102.09(9), O(1)–Ti–O(3) 115.72(9).

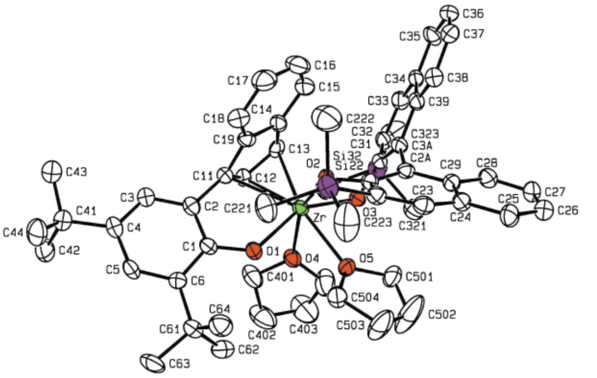

Fig. 3 Selected bond distances (Å) and angles (°) for (p-*R*,*R*)-**8**: Zr–O(1) 2.100(3), Zr–O(2) 2.017(3), Zr–O(3) 2.095(3), Zr–O(4) 2.387(3), Zr–O(5) 2.356(3), Zr–C(11) 2.531(4), Zr–C(12) 2.511(4), Zr–C(13) 2.564(4), Zr–C(14) 2.723(4), Zr–C(19) 2.696(4), O(1)–Zr–O(2) 99.1(1), O(2)–Zr–O(3) 92.6(1), O(1)–Zr–O(3) 150.5(1), O(2)–Zr–O(5) 82.25(12), O(3)–Zr–O(5) 76.0(1), O(1)–Zr–O(5) 78.8(1), O(2)–Zr–O(4) 159.0(1), O(3)–Zr–O(4) 79.2(1), O(1)–Zr–O(4) 80.3(1), O(5)–Zr–O(4) 77.1(1).

diastereoisomers. It has proven difficult to isolate crystalline products from hydrocarbon solvents. However, use of THF was found to lead to crystals of a new compound **8** shown to contain a pseudo-octahedral zirconium metal center (Figure 3). Interestingly **8** can be seen to contain a p-*R* chelated indenylphenoxide and two, cis-coordinated THF molecules along with the (*R*)-binol ligand. It is also important to note that the indenyl ring is only η^3-bound in the solid state of **8**, with significant elongation of the Zr–C(aromatic) distances (Figure 3). A similar bonding mode is also seen in **7** (Figure 2) whereas the indenyl ring in **3** (Figure 1) more closely approaches η^5-coordination.

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Notes and references

‡ *Selected spectroscopic data*. For **3**: ^{1}H NMR (C_6D_6, 25 °C): δ 6.75–7.61 (aromatics); 6.43, 6.33 (d, η^5-C*H*); 3.27, 2.49 (s, N*Me*$_2$); 1.68, 1.44 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 172.5 (Ti–O–*C*); 101.3 (η^5-*C*H). For **4**: ^{1}H NMR (C_6D_6, 25 °C): δ 6.81–7.60 (aromatics); 3.11, 2.59 (s, N*Me*$_2$); 2.22, 1.99 (s, C*H*$_3$); 1.65, 1.44 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 172.2 (Ti–O–*C*); 108.1 (η^5-*C*Me). For **5**: ^{1}H NMR (C_6D_6, 25 °C): δ 6.85–7.59 (aromatics); 6.55, 6.19 (d, η^5-C*H*); 2.91, 2.31 (s, N*Me*$_2$); 1.64, 1.44 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 171.0 (Zr–O–*C*); 95.5 (η^5-*C*H). For **6**(p-*S*,*S*): ^{1}H NMR (C_6D_6, 25 °C): δ 6.65–8.25 (aromatics); 5.44 (d, η^5-C*H*); 1.35, 1.32 (s, C*Me*$_3$); 0.42, 0.29 (s, Si*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 173.1, 165.6, 156.6 (Ti–O–*C*); 106.3 (η^5-*C*H). For **7**(p-*S*,*S*): ^{1}H NMR (C_6D_6, 25 °C): δ 6.49–8.16 (aromatics); 2.27, 1.62 (s, C*H*$_3$); 1.35, 1.22 (s, C*Me*$_3$); 0.49, 0.28 (s, Si*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 173.2, 163.8, 160.7 (Ti–O–*C*); 100.3 (η^5-*C*Me). (p-*R*, *S*): ^{1}H NMR (C_6D_6, 25 °C): δ 5.81–7.96 (aromatics); 2.24, 1.59 (s, C*H*$_3$); 1.47, 1.33 (s, C*Me*$_3$); 0.46, 0.16 (s, Si*Me*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 173.0, 168.7, 156.9 (Ti–O–*C*); 108.1 (η^5-*C*Me). For **8**(p-*R*,*R*): ^{1}H NMR (C_6D_6, 25 °C): δ 6.53–8.28, (aromatics); 5.59 (s, η^5-C*H*); 3.57 (s, O–C*H*$_2$–CH$_2$); 1.39 (s, O–CH$_2$–C*H*$_2$); 1.35, 1.26 (s, C*H*$_3$); 1.35 (s), 1.22 (s, C*Me*$_3$); 0.49 (s), 0.36 (s, Si*Me*$_3$). Selected ^{13}C NMR (C_6D_6, 25 °C): δ 171.9, 160.7 (Zr–O–*C*); 99.4 (η^5-*C*H).

§ *Crystal data*: For **3** at 150 K: $C_{27}H_{38}N_2OTi$, M = 454.52, space group $P2_1/n$ (No. 14), a = 12.4594(3), b = 11.7575(3), c = 18.0226(4) Å, β = 108.1734(13)°, V = 2508.5(2) Å^3, d_{calc} = 1.203 g cm^{-3}, Z = 4. Of the 5700 unique reflections collected ($5 \le \theta \le 27°$) with Mo–K$_\alpha$ (λ = 0.71073 Å), the 5694 with $F_o^2 > 2.0\ \sigma\ (F_o^2)$ were used in the final least-squares refinement to yield R = 0.041 and R_W = 0.099. For **4** at 150 K: $C_{29}H_{42}N_2OTi$, M = 482.57, space group $P2_1/c$ (No. 14), a = 10.0202(2), b = 13.0802(3), c = 22.0926(4) Å, β = 102.3111(13)°, V = 2829.01(19) Å^3, d_{calc} = 1.133 g cm^{-3}, Z = 4. Of the 6044 unique reflection collected ($5 \le \theta \le 27°$) with Mo–K$_\alpha$ (λ = 0.71073 Å), the 6040 with $F_o^2 > 2.0\ \sigma\ (F_o^2)$ were used in the final least-squares refinement to yield R = 0.061 and R_W = 0.160. For **5** at 150 K: $C_{27}H_{38}N_2OZr$, M = 497.84, space group $P\bar{1}$ (No. 2), a = 12.9534(3), b = 14.0719(4), c = 15.2631(4) Å, V = 2589.5(2) Å^3, d_{calc} = 1.277 g cm^{-3}, Z = 4. Of the 11660 unique reflections collected ($5 \le \theta \le 27°$) with Mo–K$_\alpha$ (λ = 0.71073 Å), the 9145 with $F_o^2 > 2.0\ \sigma\ (F_o^2)$ were used in the final least-squares refinement to yield R = 0.053 and R_W = 0.136. For **6** at 150 K: $C_{49}H_{54}O_3Si_2Ti$, M = 795.05, space group $P2_1$ (No. 4), a = 11.9436(10), b = 13.1268(10), c = 16.1538(12) Å, β = 102.861(4)°, V = 2469.1(6) Å^3, d_{calc} = 1.069 g cm^{-3}, Z = 2. Of the 7600 unique reflections collected ($5 \le \theta \le 25°$) with Mo–K$_\alpha$ (λ = 0.71073 Å), the 7586 with $F_o^2 > 2.0\ \sigma\ (F_o^2)$ were used in the final least-squares refinement to yield R = 0.087 and R_W = 0.187. For **7** at 150 K: $C_{49}H_{54}O_3Si_2Ti$, M = 823.10, space group $P2_1$ (No. 4), a = 12.0012(4), b = 13.6234(5), c = 16.3611(6) Å, β = 105.5417(14)°, V = 2577.2(3) Å^3, d_{calc} = 1.061 g cm^{-3}, Z = 2. Of the 10232 unique reflection collected ($5 \le \theta \le 30°$) with Mo–K$_\alpha$ (λ = 0.71073 Å), the 10199 with $F_o^2 > 2.0\ \sigma\ (F_o^2)$ were used in the final least-squares refinement to yield R = 0.053 and R_W = 0.148. For **8***C_7H_8*C_4H_8O at 150 K: $C_{68}H_{86}O_6Si_2Zr$, M = 1146.83, space group $P2_12_12_1$ (No. 19), a = 12.5231(3), b = 19.2231(4), c = 25.9127(6) Å, V = 2964.61(10) Å^3, d_{calc} = 1.221 g cm^{-3}, Z = 4. Of the 12567 unique reflections collected ($5 \le \theta \le 26°$) with Mo–K$_\alpha$ (λ = 0.71073 Å), the 12553 with $F_o^2 > 2.0\ \sigma\ (F_o^2)$ were used in the final least-squares refinement to yield R = 0.063 and R_W = 0.136. Flack parameters: compound **6**, 0.04(5); compound **7**, −0.01(2); compound **8**, 0.03(4). CCDC 201167–201170, 201172, 201174. See http://www.rsc.org/suppdata/cc/b2/b212724e/ for crystallographic data in .cif or other electronic format.

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